

PRODUCTION OF KERAMZIT GRAVEL USING GALVANIC SLUDGE

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The possibility of used galvanic sludge in the production of keramzit was studied. It was determined that there is a relation between the physical-chemical and operating characteristics of the porous fill and the chemical-mineralogical and phase compositions, structure and heat-treatment regime of the sludge. The migration of heavy-metal ions from the keramzit into the water extracts was studied and the technological regimes for environmentally safe production were determined.

Key words: keramzit, galvanic sludge, swellability, technological properties, structure, rheology, heavy metals, migration.

Keramzit gravel is one of the main industrially produced, porous, artificial fills. The important indicator determining the production prospects and use in construction are the cost, quality and environmental safety of keramzit. The indices are all interrelated and are determined by the bulk density of keramzit and the type of materials used.

The problem of decreasing the bulk density in the production of keramzit gravel can be solved by regulating the composition of the raw mix by introducing corrective additives simultaneously with obtaining the intermediate product with the required swellability.

In our view, galvanic sludges from the Belorussian Metallurgical Plant (BMP) and the Minsk Tractor Plant (MTP) can serve as just such an additive. They are characterized by a high content of iron oxides (12.70–58.52%³) and meet the specifications for keramzit raw material.

The BMP wastes are formed when waste waters are neutralized at the neutralization stations STPTs-1 and STPTs-2

using milk of lime. The MTP wastes are formed when waste waters are purified using a ferroferrihydrosol. The latter comprises a suspension of iron (II, III) oxyhydrates with the following composition, %: 90.3 Fe₂O₃, 9.7 FeO. The average chemical composition of the sludges, dried at 100°C, in terms of the oxides is presented in Table 1.

X-ray phase analysis established that BMP sludge consists mainly of iron and calcium compounds. The main crystal phases are CaSO₄ · 2H₂O and CaSO₄ · 0.5H₂O in STPTs-1 sludge and CaCO₃ in STPTs-2 sludge. The remaining components are present in the form of amorphous compounds. Iron oxide is found in the form of hydroxyphosphates with different compositions, determined by the ratios Fe₂O₃ : P₂O₅ : H₂O. MTP sludge does not contain crystalline phases and the compounds present in it are amorphous complex heteropoly compounds or hydrated polymers possessing molecular links, including Fe(Me)(OH)–O, as well as orthophosphate groups.

According to differential-thermal analysis (Fig. 1) of sludge dried at 100°C a complicated endo effect with a minimum in the temperature interval 160–200°C is observed in the temperature range 100–300°C. Partial degradation of

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³ Here and below, the content by weight, %.

TABLE 1. Average Chemical Composition of the Experimental Sludges

Sludge	Content, wt. %														
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Cr ₂ O ₃	NiO	CuO	ZnO	CO ₂	P ₂ O ₅	SO ₂	other
MTZ	0.47	0.21	58.52	3.73	2.22	0.02	2.48	5.22	0.04	0.08	9.44	1.10	3.43	2.67	10.37
STPTs-1	–	–	18.25	20.47	0.47	0.51	1.06	–	–	–	1.69	0.07	0.91	35.27	21.30
STPTs-2	–	–	12.67	36.92	1.01	0.30	0.98	–	–	–	3.16	9.28	18.26	0.35	17.07

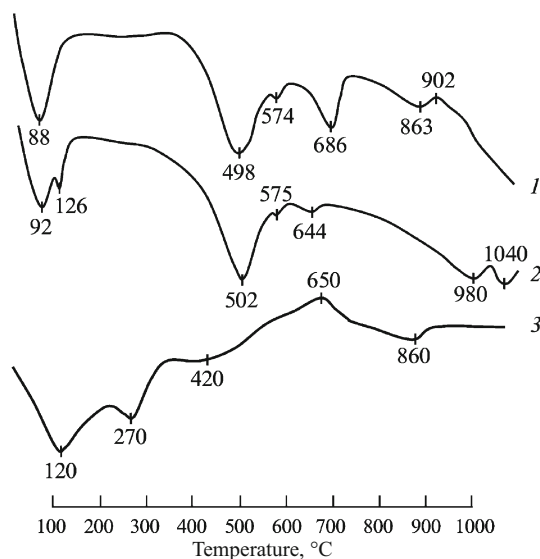


Fig. 1. DTA curves of the experimental galvanic sludges: 1) STPTs-1; 2) STPTs-2; 3) MTP.

hydroxides and hydroxide salts occurs in this temperature interval; calcium sulfate dihydrate and polyhydrate present in STPTs-1 sludge lose chemically bound water. In addition, for MTP sludge water is removed in two step (at 120 – 140 and 270 – 300°C), indicating that the bonding force of the moisture in the material is different. In the indicated temperature interval, 90 – 92% of the physically and chemically bound water splits off, and the remaining water is removed in a wide temperature interval right up to 750°C, which attests to the presence of strongly bonded OH-groups coordinated by a metal in the wastes. In the temperature interval 260 – 400°C the iron oxyhydrates decompose with α -Fe₂O₃ being formed. According to the literature γ -Fe₂O₃ gradually transforms into α -Fe₂O₃ in the temperature interval 400 – 800°C [1, 2]. An exo effect associated with a crystallization process is observed in the DTA plots at temperatures 600 – 700°C: α -Fe₂O₃ forms in the STPTs-1 and MTP sludges, while α -Fe₂O₃ and hydroxylapatite Ca₅(PO₄)₃OH forms in the STPTs-2 sludge. The endothermal effect, which is characteristic for all sludges, with maxima of different intensity in a narrow temperature interval 810 – 950°C is associated with the release of gas during the decomposition of calcium carbonates. The presence of the latter in the composition is due to the particulars of the technological process of purifying waste waters.

To study the prospects for using BMP and MTP galvanic sludge in the production of keramzit gravel and determine the optimal compositions of raw mixtures and the conditions of their swelling laboratory-technological test of this technogenic raw material were performed. BMP and MTP sludges were introduced in amounts 5 – 15% into low-melting clayey raw material from the Kustikha deposit (Gomel' Oblast'), which is the main raw material resource of the Petrikovskii Keramzit Plant of Gomel' DSK, JSC, and the Lukoml' deposit (Vitebsk Oblast') — Novolukoml'skii Keramzit Gravel Plant, JSC. Both clays are low-melting, medium-plastic, semi-acidic and highly disperse and sinter at low temperatures. The average chemical composition of the clays used is presented in Table 2.

In the laboratory 10 mm in diameter raw granules were formed by the plastic method. After drying at 100 – 105°C the granules were fired in two steps. In this method the temperature increased rapidly from the thermal preparation temperature to the swelling temperature. At the first step the temperature increased slowly to 550°C at the rate 300 K/h, and at the second step the temperature increased rapidly from 550 to 1100 – 1200°C at the rate 600 K/h. The soaking time at the maximum temperature was 10 min.

The studies showed that the introduction of galvanic sludges into the raw mixture within the experimental content range for obtaining keramzit gravel increases the porosity of the samples and decreases density, which is very important in the production of artificial porous fills. The structure with the highest density is found in samples containing the lowest amount of wastes — 5%. In such samples the porosity develops at the boundaries of clayey particles, where, in all probability, the concentration of iron oxides, introduced by the sludges, is highest. The character of the porosity changes when wastes are introduced in amounts 10 to 15%. The pores are distributed more uniformly over the volume of the material, and large voids 1 – 2 mm in size appear. However, in this case the sludges introduced in amounts > 10% decrease the swelling interval of the raw mixture, which can adversely affect the behavior of the firing process under industrial conditions.

The optimal amount of the wastes introduced was determined from an assessment of the physical-chemical and technological properties of the samples: 8 – 10% BMP, 7 – 8% MTP for compositions based on Kustikha clay and 7 – 8% BMZ, 6 – 7% MTP for compositions based on Lukoml' clay. The swelling interval for the raw mixes studied was 1130 – 1160°C.

TABLE 2. Average Chemical Composition of the Clays Used

Clay	Content, wt. %								
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	other
Lukoml'	55.2	14.09	0.99	7.51	3.11	5.6	2.27	2.27	8.95
Kustikha	65.3	16.04	0.82	4.70	1.39	1.57	0.35	1.45	8.07

Keramzit obtained from these compositions was sent for testing to the laboratory of the Novokoml'skii Keramzit Gravel Plant where the following were determined: the bulk density, granulometric composition and crush and freeze resistances of the porous fill. The tests showed that with respect to all control parameters the material meets the CTB specifications. After 20 freeze-thaw cycles the mass losses are 0.83% and the crushing strength is 3.9 N/m^2 , which is significantly higher than the same indices for samples synthesized using clays without galvanic sludge added.

Analysis of the microstructure of the materials obtained, which is shown in Fig. 2, shows that the keramzit gravel samples possess a complex irregular structure. Individual pores differ in shape, orientation and surface curvature. The predominant pore size is $0.1 - 0.2 \text{ mm}$.

X-ray phase analysis shows that the phase composition of the keramzit obtained is represented by α -quartz, mullite and hematite.

In the case of accelerated firing of keramzit gravel iron oxide Fe_2O_3 , which has a determining influence on the swelling of the material, is formed at temperatures $500 - 700^\circ\text{C}$ and remains in an oxidative atmosphere up to $1000 - 1100^\circ\text{C}$. Porization of the material occurs in a narrow temperature interval $1130 - 1160^\circ\text{C}$ as a result of the reduction of iron oxides by CO and H_2 , which are released from clayey minerals and organic substances as well as with the decomposition of carbonates CaCO_3 [3].

The slip method of processing the raw material requires slip with good flowability and fluidity and minimal moisture content. For this, the rheological characteristics of slips in the system clay – galvanic sludge – water were studied and the conditions for thinning the clay suspension based on the optimal raw mixture were determined. Thinners which are well-known in the industry were used as electrolytes: soda ash Na_2CO_3 , liquid glass Na_2SiO_3 , sodium pyrophosphate $\text{Na}_4\text{P}_2\text{O}_5$, sodium tripolyphosphate $\text{Na}_2\text{P}_3\text{O}_{10}$ and lignin-alkaline reagent (LAR). The electrolytes were introduced with the following concentrations: 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5% and so forth above 100% of the dry mass. The moisture content and density of the slip were 54% and 1530 kg/m^3 .

The changes in the viscosity and thickening factor of slip containing different quantities of electrolyte were determined from the rate of efflux from the funnel of an Engler viscosimeter after 30 sec and 30 min holding times.

The studies showed that it is undesirable and ineffective to introduce individual electrolytes (soda ash, liquid glass, sodium tripolyphosphate and lignin-alkaline reagent) into the slip, since the transition of the system from structured to Newtonian flow is not observed or occurs at high electrolyte content, which is due to the polymineral nature of the clayey raw material as well as the composition of the galvanic sludges.

The required technological properties of slip in the system clay – galvanic sludge – water can be obtained only by

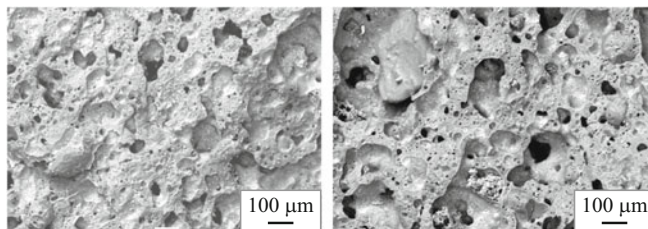


Fig. 2. Microstructure of keramzit gravel samples.

using combinations of electrolytes, for example, soda ash in combination with sodium tripolyphosphate. Combining electrolytes makes it possible to lower the moisture content significantly (to 48 – 49%), the thickening factor (to 1.1) and the efflux time (to 6 sec) of the slip. In this case the effective combined influence of the electrolytes on the properties of slip is due to the different directionality and mechanism of their action, which confirms the appearance of synergism (intensification of the action of the components when they are introduced simultaneously) and changes the rheological character of the flow of the clayey suspension from structured to Newtonian.

The problem of the adverse impact of heavy metals on the environment during the reprocessing of wastes and during usage of the ready materials obtained on their basis remains urgent. It is known that keramzit gravel and the blocks based on it are exposed to the weather and subject to mechanical damage and other factors arising in finished and unfinished buildings and destroying the integrity of the construction and allowing heavy-metal ions to migrate out of the building material. Possessing high biological and migration activity they enter surface and ground waters, accumulate in plants and create an indirect hazard to humans. The level of migration of chemical elements from keramzit gravel obtained using galvanic sludge was studied in this connection.

Migration was investigated using guidelines [4] for sanitary-hygienic evaluation of construction materials to which industrial wastes have been added. The solution (extracts) for determining the level of migration of chemical elements were prepared by isothermal soaking of experimental samples in the form of 10 mm in diameter granules in a model medium (distilled water) at temperatures 20 ± 2 and $40 \pm 2^\circ\text{C}$. The exposure times were 1, 3, 7, 10, 20 and 30 days. Since keramzit gravel is subjected to periodic short-time contact with atmospheric precipitation, the sample : model medium volume ratio was 1 : 3. The studies were performed on keramzit samples with very small cleavage surfaces comprising 8 – 10% of the sample surface, which made it possible to simulate some breakdown of the material during usage.

According to chemical analysis of the sludges (Table 1) iron, lead and zinc can leach from keramzit gravel. In this connection the concentrations of the indicated cations in the water extracts were determined by atomic-adsorption spectroscopy. The migration of heavy-metal ions was studied with a GBC PAL 3000 Auto Sampler Avanta GM (USA) in

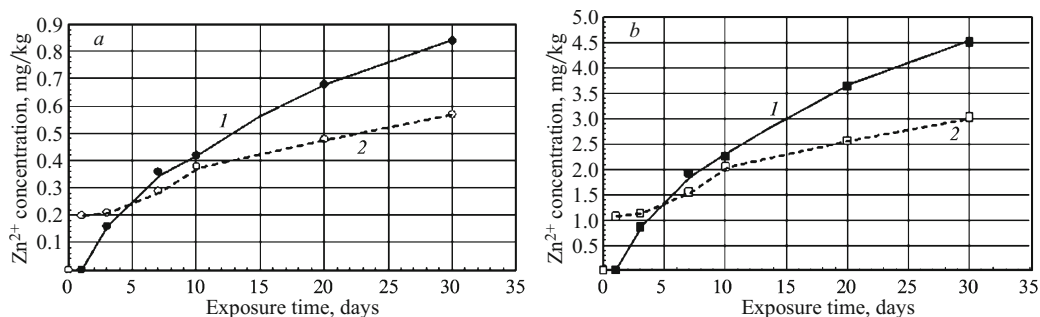


Fig. 3. Concentration of Zn^{2+} ions in water extracts (a) and soil (b) versus the exposure time: 1 and 2) exposure temperatures 40 and 20°C, respectively.

argon gas at the wavelengths 283.3, 392.0 and 307.6 nm for lead, iron and zinc, respectively.

The possible adverse environmental effects of heavy-metal ions were evaluated by comparing their actual content in the water extract to their maximum admissible content in soil and household and public drinking water (GN 2.1.5.10–21–2003 [5]).

The results showed that increasing the exposure time from 1 to 30 days and the soaking temperature from 20 to 40°C does not cause lead (Pb^{2+}) and iron (Fe^{2+} , Fe^{3+}) to migrate out of the ceramic sample. In our opinion, this phenomenon can be explained by strong fixation of these ions in the structure of the material. According to x-ray phase analysis iron ions are present in the crystalline phase of hematite $\alpha\text{-Fe}_2\text{O}_3$, the Fe–O bond being characterized by quite high rupture energy (410.5 kJ/mole). The absence of migration of lead ions can be explained by low lead content in the ceramic paste (0.006% in terms of the oxide PbO) and by fixation in the glassy phase of the material.

The dependence of the migration of zinc ions on the exposure time and temperature is presented in Fig. 3. At 20°C the zinc ions Zn^{2+} in water extracts are identified starting at 3 days of soaking; their concentration is 0.16 mg/liter. It was determined that about 50% of the zinc ions from the total amount of migrating ions leach out during the first 10 days, and subsequently the migration rate decreases and equals 20% on average. Increasing the exposure temperature from 20 to 40°C increases the concentration of the experimental ions significantly already during the first day to 0.2 mg/liter, which is 35% of the total number of migrating ions. About 20% Zn^{2+} migrate during 10 day soaking; their concentration is 0.38 mg/liter.

As one can see from the plot presented, at soaking temperatures 20 and 40°C the concentration of Zn^{2+} ions in water extracts is in the range 0 – 0.84 mg/liter depending on the exposure time, which does not exceed the MAC, equal to 1 mg/liter.

The higher level of migration of zinc ions compared with Fe^{2+} and Fe^{3+} can be explained by the relatively low values of the rupture energy of the Zn–O bond, equal to 275 kJ/mole. In addition, on the basis of the investigation of the structure

and phase composition of the material developed it was determined that zinc is present predominately in an amorphized phase or adsorbed on phase interfaces and, in consequence, it is more mobile than ions occupying crystal lattice sites.

On the basis of the studies performed the migration of ions of heavy elements from a sample into distilled water can be explained by a complicated set of physical-chemical processes occurring at solid – liquid interfaces, among which the diffusion of ions, hydrolysis of salt of polysilicic acids and, to a very small degree, dissolution. As result of diffusion and chemical processes occurring simultaneously mixed complex compounds, including the ligands H_2O and HO^- , in which the heavy-metal ions are complexing agents, are formed. Apparently, the growth of the migration level of Zn^{2+} ions with the exposure temperature increasing from 20 to 40°C is explained by intensification of the physical-chemical processes considered as well as by a decrease of the viscosity of the model medium.

The soil concentration of the ions studied was determined by standard computational methods. The ions Fe^{2+} , Fe^{3+} and Pb^{3+} were not found. The dependence of the Zn^{2+} concentration in soil on the exposure temperature and time (Fig. 3) shows that the content of these ions is 0 – 4.512 mg/kg, while the MAC is 23 mg/kg. The data obtained correlate completely with the values of the migration of the ions studied into water extracts.

It can be concluded on the basis of an analysis of the data obtained that an increase of the number of heavy-metal ions in water extracts is noted only for zinc, and its content satisfies completely the specifications in the regulatory documents concerning the content of chemical elements in soil and household and public drinking water.

In summary, the use of sludge from the Belorussian Metallurgical Plant and the Minsk Tractor Plant as corrective additives in the production of keramzit will make it possible not only to obtain a material with the required swellability and improve the quality of the porous fill but also to extend the regulation range of its properties. Keramzit obtained using BMP and MTP sludge is environmentally safe and characterized after 20 freeze-thaw cycles by mass losses

0.83%, crushing strength 3.9 N/m² and content of water-soluble sulfur and sulfate compounds no more than 0.2%.

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